CLOSED TUBE TEST (CARIUS TUBE TEST)

MEASUREMENT RESULTS AND INTERPRETATION

FOR THE THERMAL DECOMPOSITION OF

THE FORMATION OF AUTOMATE YELLOW 96

To: US Chemical Safety & Hazard Investigation Board
2175 K Street N.W.
4th Floor
Washington, DC 20037

F.A.O. : Mr. David Heller

Prepared By: ....
David Y. Kohn
Laboratory Technician
Process Evaluation

Approved By: ....
Charles W. Gilbert
Sr. Chemist

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

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SUMMARY

This report presents the results of Carius tube testing for a reaction mixture of 1eq 2-Chloronitrobenzene and 1.83eq 2-Ethylhexylamine to form Automate Yellow 96. This Carius tube test was used to characterize the thermal stability of this reaction by heating it from ambient temperature to 400°C while searching for any pressure generation and/or thermal activity.

The sample was weighed into the tube, connected to the apparatus and ramped over the given temperature range. There were two exothermic responses starting at 37.7°C and 192.0°C respectively. The maximum pressure rise of 14.34 bar min^{-1} occurred, which is very large. The tube burst at 58.7 bar and 345.8°C.

TEST STANDARD

Test performed according to ABPI 6.3 Guideline for Chemical Reaction Hazard Evaluation.

TEST PURPOSE

The purpose of the test is to clearly identify exothermic activity in the sample as a function of temperature. The sample may be a reagent, reaction intermediate or reaction product. It may be any portion of the reaction mass under investigation. This screening test provides some guidance as to both the magnitude and onset of any such exotherm and associated gas generation and vapor pressure effects.

TEST PRINCIPLE

A quantity of sample (normally 10 grams) is sealed in a glass Carius tube and placed in a furnace that is heated at 0.5 K/min. The temperature at the center of the sample and the pressure in the tube are monitored and any exothermic activity logged using a microcomputer.

TEST SENSITIVITY

The test is capable of detecting changes in the sample ramp rate of between 5 and 10 K/hr above that of the furnace rate. This corresponds to a sensitivity of 3 to 10 W/kg.

TEST APPARATUS

The Carius tube is a Pyrex® glass tube (35 mL) with a re-entrant thermocouple pocket and an adapter at the outlet with a glass-to-metal seal. The outlet is connected via a stainless steel tube with a capillary bore to a calibrated 100 bar pressure transducer. The capillary tube is filled with silicon oil to reduce the void space available for vapor condensation outside the Carius tube.

The Carius tube is situated in a furnace (that can withstand rupture of the tube and burning of contents) and the furnace temperature is ramped at 0.5 K min^{-1} from ambient to 400°C (673 K).

Microprocessor data logging, which has the flexibility to cope with a wide range of gas pressures and temperatures within an experiment, is used to monitor the temperature at the center of the sample, the oven temperature and the pressure in the sample tube.

The equipment is represented in **Figure 1**. A typical reaction trace showing exothermic activity and gas generation is shown in **Figure 2**.

DATA INTERPRETATION

The onset temperature for an exotherm (or endotherm) is indicated by a deviation in the rate of rise of sample temperature from the rate of rise of the oven temperature. In the plot of differential temperature against oven temperature, both the peak height and area under the exotherm curve are indicative of the magnitude of exothermic activity. The former indicates the rate at which the sample is generating or absorbing heat. The later indicates the quantity of heat liberated or absorbed. An indication of gas generation is given by the Antoine plot, which is a plot of logarithm of sample pressure (corrected for air pressure in the sample tube) against reciprocal of absolute temperature. Vapor pressure effects approximate to a straight line on such a plot and any upward deviation is indicative of permanent gas evolution.
It is imperative that safety factors are used when relating screening test data to the large scale plant. Typically, a safety factor of 50°C, but up to 100°C is applied to the onset temperature, that will depend on the scale on which the material is to be handled and stored. A minimum safety factor of 50°C is recommended for small scale storage or handling. If the material is to be

stored or handled at a temperature near its thermal onset (including a safety factor), it is recommended that further tests be conducted under low heat loss conditions to more accurately quantify a safe maximum exposure temperature. The slow heating rate used in the Carius tube test produces a much more accurate definition of onset temperature than that which would be obtained at higher heating rates. For this reason, the safety factor applied to Carius tube onsets is 50°C in most cases. When data gained at higher heating rates (2 K/min or higher) is interpreted, safety factors of up to 100°C are commonly used.

SAMPLE INFORMATION AND TEST CONDITIONS:

Client:	US Chemical Safety & Hazards Investigation Board
Reaction:	Formation of Automate Yellow 96 with 1eq of 2-chloronitrobezene and 1.83eq of 2-etheylhexylame
Source of Reactants:	Aldrich
Job Number:	2713B
Test Date:	4/26/00
Filename:	CNA2713E/F.ASC

Deviations from Standard Test and/or Equipment: None

Start Temperature:	19.56°C
Start Pressure:	0.0 barg
Ramp Rate:	0.5 K/min
Weight of 2-Chloronitrobenzene:	5.9571g
Weight of 2-Ethylhexlyamine:	8.9487g
Total Sample Size:	14.9058g
Initial Appearance:	Fine yellow powder with clear liquid. The liquid became yellow upon addition to the 2-Chloronitrobenzene
Final Contents Appearance:	Tube burst

RESULTS:

Data on the First Exotherm

Onset Temperature(s): 37.7°C

Maximum Delta Temperature: 11.7°C

Data on the Second Exotherm

Onset Temperature(s): 192.0°C

Maximum Delta Temperature: 129.9°C

Ultimate Conditions Reached in the Test

Largest Rate of pressure Rise: 14.34 bar min^{-1} at 295.7°C

Ultimate Pressure: 58.7 barg at 345.8°C

Final Conditions

Temperature: 345.8°C

Pressure: 58.7barg

Time (when oven temp. is max): 7.0 hours

Cool-Down Conditions

Temperature: Tube burst

Pressure:

Gas Generation

#Volume of Permanent Gas (per gram of reaction mixture) at STP	Tube burst
#Peak Rate of Gas Generation ($cm^3\ min^{-1}g^{-1}$ based on the peak pressure rate corrected to STP)*	15.94 based on 14.34 bar min^{-1}
Onset of Permanent Gas Generation (°C / based on the Antoine Plot)	140.2°C and 256.1°C
	Exotherm 1 Exotherm 2

* This number is very large.

Comments: Tube burst at 345.8°C.

CALCULATIONS

Calculation of the Volume ($cm^3 g^{-1}$) of Permanent Gas (per gram of reaction mixture) at STP

$P_{STP}V_{STP} / T_{STP} = P_{EXP}V_{EXP} / T_{EXP}$ (for ideal gas)

From the cool-down conditions we calculate the right hand side of the above equation (keeping in mind to correct the cool-down pressure for the pressure in the tube at the start of the experiment):

$P_{EXP} = (P_{cool} – P_{start})/ 1.01325$ and V_{EXP} = Carius tube volume, 35 cm^3 and $T_{EXP} = T_{cool}$

where T_{cool} is the temperature (K) upon cooling down, P_{cool} is the pressure in the tube upon cooling down (bar), P_{start} is the pressure in the tube at the start of the test (ambient), 35 cm^3 is the Carius tube volume, 1.01325 is the conversion factor between bar and atm units and STP conditions are 1 atmosphere and 273.15 K.

V_{STP} (as obtained above) is divided by the sample weight to get the final units ($cm^3 g^{-1}$).

Peak Rate of Gas Generation (cm^3 $min^{-1}g^{-1}$ based on the peak pressure rate corrected to STP)

Peak Rate of Gas Generation = { (dP/dt / 1.01325) x 35 cm^3 x (273.15 / T) } / (mass in grams)

where dP/dt is the maximum rate of pressure rise observed during the test and T is the sample temperature (K) at the maximum rate of pressure rise.

DISCUSSION

The time-temperature-pressure profile obtained on the sample is shown in **graph 1**.

The ultimate pressure reached in the test was 58.7 barg and occurred at 345.8°C at which point the tube burst. An examination of the differential temperature plot (**graph 2**) reveals two exothermic responses at 37.7°C and 192.0°C, respectively. This first exothermic response is due to the heat of reaction for the formation of Automate Yellow 96 and the second exothermic response is due to it's decomposition. The Antoine plot (**graph 3**) reveals two upward deviations from the vapor pressure curve with onsets at 140.2°C and 256.1°C which correspond to exotherm 1 and exotherm 2, respectively. The peak rate of gas generation was 15.94 cm^3 min^{-1} g^{-1}. This number was based on 14.34 bar min^{-1} at 295.7°C. This is a very large quantity. The tube burst at 345.8°C and 58.7 bar.

A safety factor of 50 °C is normally used to specify safe plant operation temperatures. However it must be kept in mind that this is a screening test and larger scale isothermal or adiabatic testing may be required to fully characterize the decomposition exotherm.

CONCLUSION

The sample underwent two exothermic events at 37.7°C and 192.0°C. There was permanent gas generation that proceeds at a very small rate starting at 140°C which corresponds to the first exotherm, and a fast rate at 256°C which corresponds to the second exotherm. The first exotherm at 37.7°C is due to the reaction while the second exotherm is the rapid decomposition of products.

Given a safety factor of 50 °C, safe plant operation for this sample is taken to be any temperature below 142°C. The normal operation temperature for the final heating stage is 150°C, which is above the safe plant operation temperature of 142°C. However, this testing does not investigate the nature of the sample under 'storage' conditions where it would be held at a given temperature for long periods of time. If storage of this material at or near its safe handling temperature is expected further testing is recommended. Specifically, an isothermal stability test.

Laboratory Screening Tool for Thermal Stability
The Carius Tube Test Apparatus

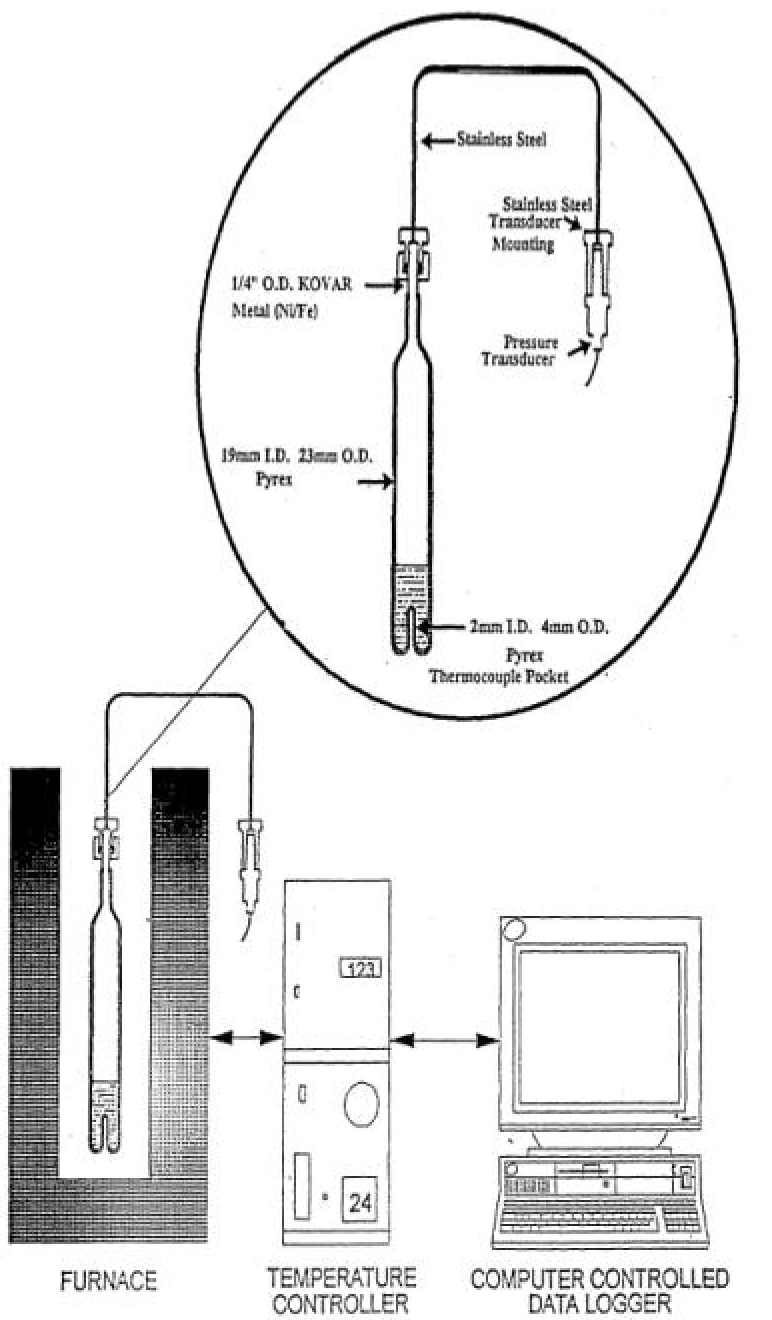


Fig. 1 - CARIUS TUBE SCREENING TEST

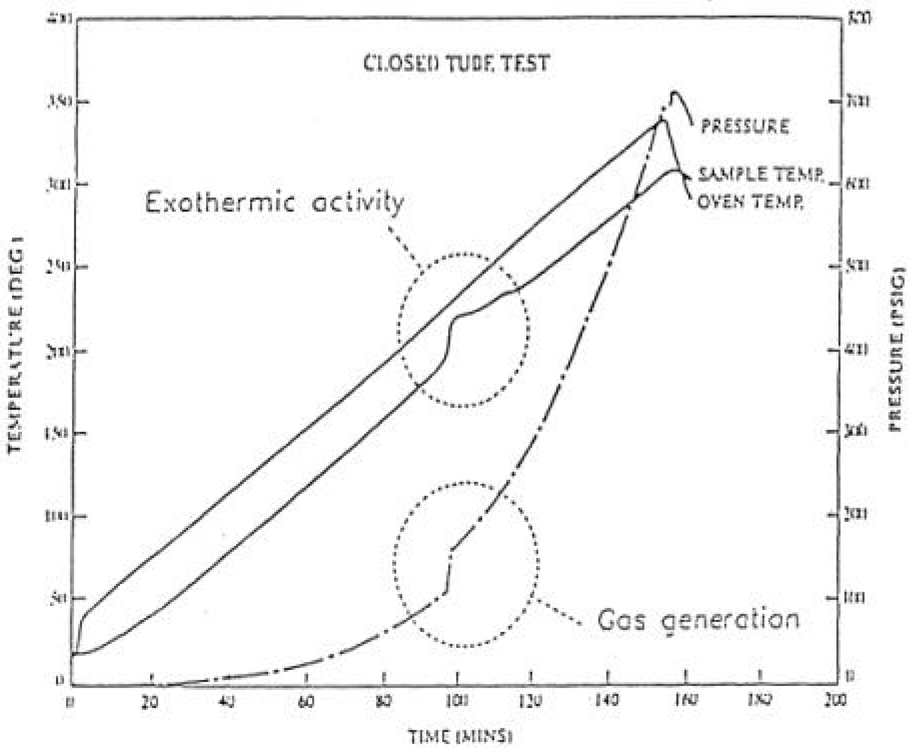
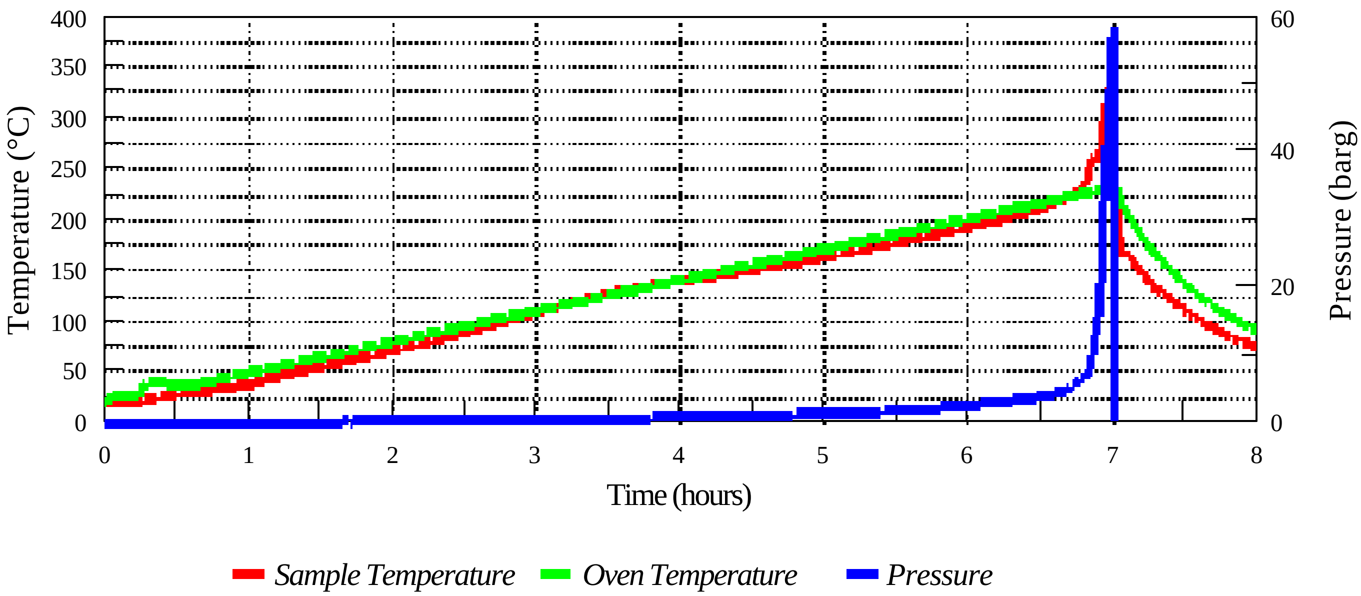


Fig. 2 - Carius tube experimental trace

GRAPH 1: US CHEMICAL SAFETY & HAZARDS INVESTIGATION BOARD

1eq 2-Chloronitrobenzene and 1.83eq 2-Ethylhexylamine-Carius Tube Screening Test



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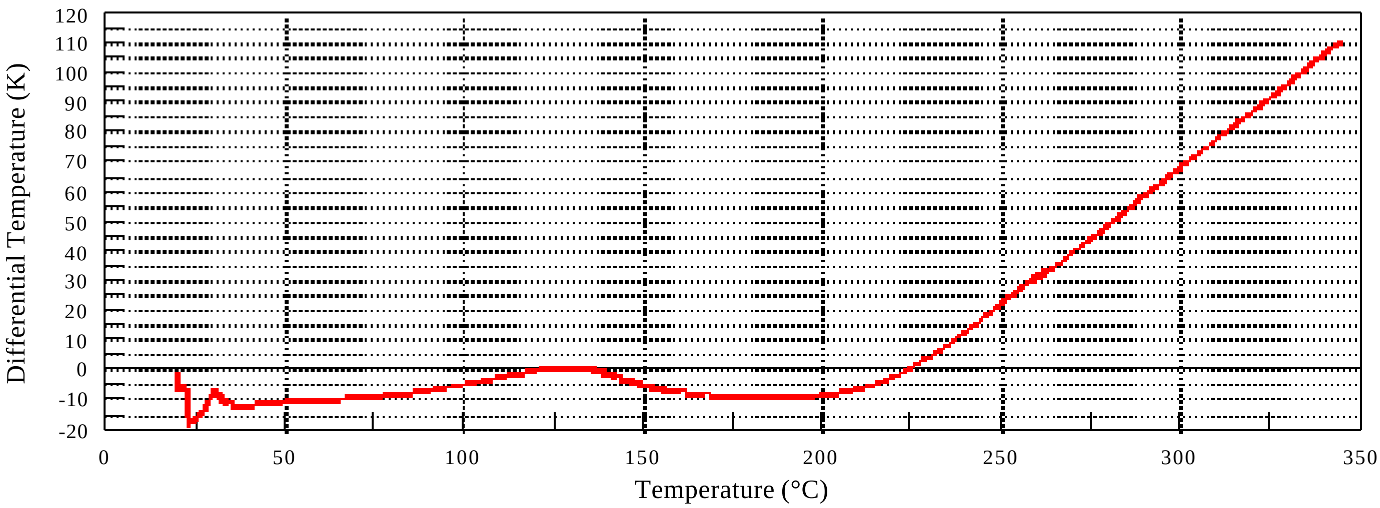
GRAPH 2: US CHEMICAL SAFETY & HAZARDS INVESTIGATION BOARD

1eq 2-Chloronitrobenzene and 1.83eq 2-Ethylhexylamine-Carius Tube Screening Test



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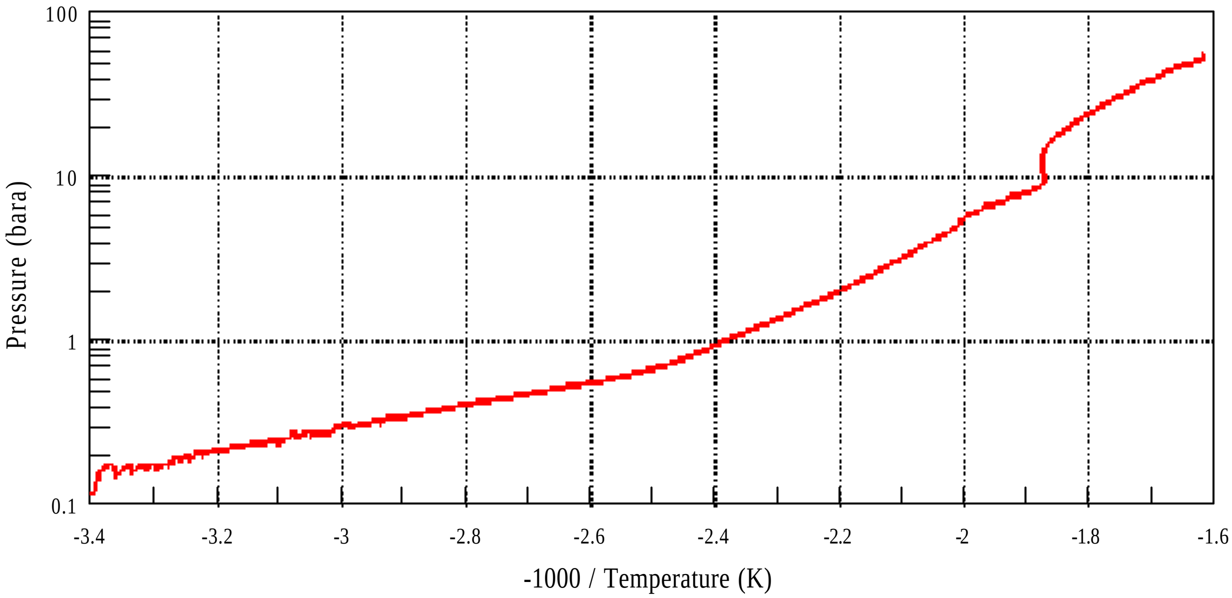
GRAPH 3: US CHEMICAL SAFETY & HAZARDS INVESTIGATION BOARD

1eq 2-Chloronitrobenzene and 1.83eq 2-Ethylhexylamine-Carius Tube Screening Test



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